Notes

Determination of Barium Ions in River-Water Samples by Inductively Coupled Plasma-Atomic Emission Spectrometry after Preconcentration by Solvent Extraction

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The maximum cotaminant level (MCL) for barium (1 mg l^{-1}) has been established in the national interim primary drinking water regulations. Soluble barium salts are known to be toxic when ingested into the body or when external exposure occurs.

The extractions of barium with hexafluoroacetylacetone¹, 18-crown-6², and polyethylene glycol³ have been reported.

The present authors studied a method based on solvent extraction with 2-thenoyltrifluoroacetone⁴ (abbreviated as TTA) and subsequent inductively coupled plasma-atomic emission spectrometry (ICP-AES) of barium. TTA is available at a reasonable cost, and the extraction procedure with TTA is simple. Barium was quantitatively extracted with 0.5 M TTA in MIBK from a solution adjusted to pH 10.0 with NH_4OH . Then 0.2 M hydrochloric acid was added and barium ions were back-extracted. The aqueous phase was injected into the ICP. The present method has been applied to the determination of barium in river-water samples.

Experimental

Reagents

Standard barium solution. A standard solution (1 mg ml^{-1}) of barium was prepared by dissolving 1.523 g of reagent-grade barium chloride, anhydrous in 1 M hydrochloric acid.

TTA solution. A TTA solution (0.5 M) was prepared by dissolving TTA (Dojindo Laboratories) in 4-methyl-2-pentanone (MIBK).

All of the other reagents were of analytical reagent grade.

Apparatus

An inductively coupled plasma atomic emission spectrometer (Shimadzu ICPQ-100) was used. The RF-power was supplied with a built-in 27.12 MHz generator. The ICP conditions are listed in Table 1.

Table 1 Operating conditions for ICP-AES

Power	1.2 kW
Ar flow rate	10.5 l/min (coolant) 1.5 l/min (plasma) 1.0 l/min (carrier)
Observation height	15 mm above the load coil
Integration time	20 s
Analytical line	Ba 455.4 nm

pH meter: a pH meter, Model M-7 Horiba Manufacturing Co., was employed.

Experimental procedure

Each test sample of 100 ml was adjusted to pH 10.0 with 7 M NH_4OH . In a separatory funnel, 10 ml of a 0.5 M TTA MIBK solution and 100 ml of a sample solution were mixed. The funnel was then shaken for 10 min with an electric shaker. After the two phases had separated, the aqueous solution was extracted. The organic phase remaining in the funnel was treated with 10 ml of 0.2 M hydrochloric acid in order to back-extract the barium ions in the organic phase. The concentration of barium back-extracted into the hydrochloric solution was determined by ICP-AES.

Results and Discussion

Effect of diluents

MIBK and benzene were tested as diluents. The recovery of barium at pH 10.0 was 94% and 2.2% with MIBK and benzene, respectively. Hence, MIBK was preferred as the diluent.

Effect of TTA concentration

Barium was extracted at pH 10.0 with 10 ml of 0.5 M TTA in MIBK. Because the recovery of barium was 46.6, 92.5, 93, 93 and 93% with 0.01, 0.05, 0.1, 0.2 and

Table 2 Recovery of metals in solvent extraction

Ion	Added/mg l ⁻¹	Found/mg l ⁻¹	Recovery, %	Ba/mg l ⁻¹		
				Added	Found	Recovery, %
Mg	5	3.1	62	0.1	0.096	96
Ca	20	8.2	41	0.1	0.093	93
Na	10	0.6	6	0.1	0.095	95
Al	2	0.04	2	0.1	0.093	93
Fe	2	1.5	75	0.1	0.098	98
K	2	0.06	3	0.1	0.095	95

Fig. 1 Effect of pH on recovery of barium. Sample, 100 ml (Ba 0.1 mg/l); 0.5 M TTA MIBK solution, 10 ml; 0.2 M HCl, 10 ml.

0.5 M TTA respectively.

Effect of pH on the recovery of barium

Measure out 100 ml of the sample containing 0.1 mg barium into a quartz beaker and adjust each pH to the 7–12 range. Transfer each solution to a funnel and treat as described above. From Fig. 1 the optimum pH for the recovery of barium was 10.0.

Co-extracted ions

Alkali and alkaline earth elements, iron and aluminum, were co-extracted with barium (Table 2).

Effect of diverse ions on the determination of barium

For the purpose of applying the present method to the determination of barium in river-water samples, the interfering effect of various metal ions on the determination was studied. Barium of 0.1 µg ml⁻¹ was extracted from a solution containing various metal ions by the above-mentioned method. The amount of metal ions added was approximately fifty-times that of the river-water sample. Magnesium, sodium, aluminum, iron, and potassium were tolerated at a ratio of 1 : 1000, 1 : 5000, 1 : 500, 1 : 500, and 1 : 500, respectively, as shown in Table 3. However, although calcium ions had an influence of 18% on the determination of barium at a

Table 3 Effect of coexisting ions on the determination of barium

Ion	Added/mg l ⁻¹	Ba/mg l ⁻¹	
		Added	Found
Mg	100	0.1	0.106
Ca	500	0.1	0.118
Na	500	0.1	0.100
Al	50	0.1	0.106
Fe	50	0.1	0.106
K	50	0.1	0.103

Table 4 Analytical results for barium in river-water samples

Added/mg l ⁻¹	Found/mg l ⁻¹	Recovery, %
0	0.010	— (n=3)
0.1	0.102	92 (n=5)

Sample was taken from Shinano River, Niigata City.
Sample: 100 ml.

ratio of 1 : 5000, calcium ions were extracted at only 40% and the concentration of the calcium ions in water was about 10 mg l⁻¹, calcium was tolerated at a ratio 1 : 500.

Analysis of the environmental sample

After filtering, we added known amounts of barium to river-water samples and measured the recovery of barium according to the previously outlined procedure. The analytical results are given in Table 4. The recovery of barium by this method was 92% and the relative standard deviation was 4.7%. The detection limit was 0.0006 mg l⁻¹ according to the expression $\{3 \times \sigma_B \times C / (\bar{X}_S - \bar{X}_B)\}$, where C is the concentration of barium, $\bar{X}_S$ is the mean emission intensity of the sample, and $\bar{X}_B$ is the mean emission intensity of the blank.

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